

Coordination Polymers

This book on coordination polymers comes onto the market at the right time and has been eagerly awaited by insiders in the field. It has been written by a young dynamic team of authors who are familiar with this research area and have wide expertise. As the authors state in their introductory chapter, the number of papers on metal-organic frameworks and coordination polymers has increased enormously over the past 15 years. At this stage, it was time to take a step back from the wealth of publications and provide a systematic overview of this research area.

In accordance with the overall structure of the book, the literature references are given at the ends of the individual chapters. This limits the number of citations for each chapter, but it also gives rise to repetitions, so that some papers are cited several times throughout the book. However, a positive aspect is that the literature is classified and, for each chapter, is very complete and representative of the state of the art at the time of publication. It must be noted that the examples described are almost entirely limited to transition metal ions and f-block elements, whereas elements of the s and p blocks are not covered, despite the fact that some reviews of those already exist. The authors argue that the compounds are either too ionic or too covalent to allow reversible formation of supramolecular bonds. This deliberate choice by the authors is reasonable, since the examples and systematic studies in the recent literature concentrate predominantly on d-block metal ions. The book contains many useful illustrations which help one to understand the text.

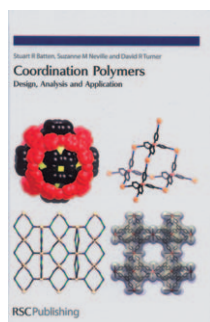
In Chapter 1, the authors present the basic knowledge needed to read through the book. This also serves as a short introduction to the field, which is aimed at student readers and beginners. As well as sketching the history of the field, the chapter gives definitions, describes typical synthetic methods, and summarizes the topics to be covered in the following chapters. Chapters 2 and 3 deal with the systematic description of structures of coordination polymers, beginning with simple structures and then discussing interpenetrated complicated compounds. To understand these structures, illustrations are very important and the authors generally make effective use of this tool. The only negative aspect is the absence of color in this book, as the pictures, schemes, etc. use only a range of gray scales, which are not very helpful for depicting multiple interpenetrated structures.

Chapter 4 deals with the “malleability” of coordination polymers. The title of the chapter

might not be clear at first sight—it deals with the multitude of possible structures that can be formed from the building blocks of which coordination polymers are constructed. The resulting polymorphism and supramolecular isomerism phenomena are described in detail, with representative examples and important principles drawn from the literature. The malleability of the individual building blocks is also described, including aspects such as the coordination number of a metal ion as a function of the oxidation state, or the connectivities of ligand molecules. The synthetic aspects treated in this chapter focus on the variables that influence which particular structures are formed. Special attention is devoted to the influence of the solvent and of the counter-ion, whereas the effects of guest molecules are only mentioned briefly. A subchapter deals with the influence of weak interactions such as hydrogen bonding, π - π interactions, and metal-metal contacts, citing relevant examples. These first four chapters provide the reader with the toolkit for mastering the definitions, the descriptions, and the rules that govern the construction of coordination polymers, at least theoretically. These chapters can be recommended as a basis for student tutorials, and also as an introduction and general overview for PhD students beginning their research and for others entering the field.

The next chapters describe representative examples of coordination polymers. Thus, the sixth chapter is devoted to transition metal compounds, with examples having coordination numbers 2, 3, 4, or 6. These mainly involve N-donor ligands, such as cyanides, pyridine derivatives, and five-membered nitrogen heterocycles. Different aspects, such as connectivity, functionality, ligand size, and aromaticity of the ligands are discussed separately. Among the O-donor ligands, nitrogen oxides and carboxylate ligands are chosen for a thorough presentation, whereas ligands with mixed donor atoms and coordination polymers with two or more ligands are only touched on briefly. Another chapter collects examples of coordination polymers with larger coordination numbers, with a main focus on lanthanides, again classified according to ligand types. There are fewer examples for each particular type of ligand than in the chapter on the transition metals, but more ligands are included, with anionic and O-donor ligands playing an important role in the formation of coordination polymers containing f-block elements. The mixed-metal 3d/4f coordination polymers are especially important, as they combine the properties of both metal ion types. Compounds of the actinides are only briefly mentioned.

A separate chapter is devoted to organometallic coordination polymers that involve metal-carbon interactions, while Chapter 8 deals with inorganic-organic hybrid materials, in which a



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metal oxide appears to play an important role as a substructure in the coordination polymer.

In the examples cited up to this point, the structural variety of the compounds has been the center of attention, and potential applications have only been hinted at. The next three chapters focus more on the properties that can be obtained by tuning of coordination polymer networks. Of the properties that have been investigated closely up to now, separate chapters deal with magnetism, porosity, chirality, and properties obtained with non-centrosymmetric compounds. For all of these, examples are given and the current systematic approaches towards achieving the desired properties are described in detail. Chapter 12 discusses the chemical reactivities that can be obtained with coordination polymers, mostly in the solid state, for example in catalytic applications. Other properties appear to have been much less explored, and these are collected together in Chapter 13, with brief highlights on luminescence, redox activity, conductivity, negative expansion coefficients, and multifunctionality. These last chapters are highly interesting for materials scientists, as they can be helpful in the design and synthesis of new functional devices.

Some of the chapters are shorter than others and have fewer citations, giving the reader an indication of the importance of ongoing research in the field. They show that a lot of work is still needed, and is already under way, to better control and tune the properties of such coordination polymers. The book nicely shows the huge variety of compounds that already exist, as well as emphasizing the potential of coordination polymers as new materials. There is still enormous scope for research in the field, and the reader will be inspired to develop new ligands, and to explore more of these compounds in order to gain better control over structures and properties.

This book can be recommended to everyone active or interested in the field. It gives an excellent overview of the current state of the art, and it is certainly a must for every university library.

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